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Internationales BüroINTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE  
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

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| <b>(51) Internationale Patentklassifikation <sup>7</sup> :</b><br><b>H01L 21/00</b>   |  | <b>A2</b>   | <b>(11) Internationale Veröffentlichungsnummer: WO 00/67299</b>                 |
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| <b>(30) Prioritätsdaten:</b><br>199 20 322.9      3. Mai 1999 (03.05.99)      DE<br>199 27 962.4      18. Juni 1999 (18.06.99)      DE  |  | <b>Veröffentlicht</b><br><i>Ohne internationalen Recherchenbericht und erneut zu veröffentlichen nach Erhalt des Berichts.</i>                |   |
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| <b>(54) Title:</b> METHOD FOR GENERATING DEFECTS IN A GRID SUPPORT OF A SEMICONDUCTOR MATERIAL  |  |   |   |
| <b>(54) Bezeichnung:</b> VERFAHREN ZUM ERZEUGEN VON DEFEKTEN IN EINER GITTERSTRUKTUR EINES HALBLEITERMATERIALS  |  |   |   |
| <b>(57) Abstract</b><br><p>In order to precisely control grid defects in a semiconductor material in a simple and cost-effective manner, the invention provides a method for generating defects in a grid support of a semiconductor material, during the thermal treatment of said material. The concentration and/or distribution of defects or blank sections is controlled in conjunction with a process gas atmosphere.</p>                        |  |   |   |
| <b>(57) Zusammenfassung</b><br><p>Um auf einfache und kostengünstige Weise eine genaue Steuerung von Gitterdefekten in einem Halbleitermaterial zu ermöglichen, ist ein Verfahren zum Erzeugen von Defekten in einer Gitterstruktur eines Halbleitermaterials während dessen thermischer Behandlung vorgesehen, bei dem die Defekt- bzw. Fehlstellenkonzentration und/oder-verteilung in Abhängigkeit von einer Prozeßgasatmosphäre gesteuert wird.</p> |  |   |   |

FORM PTO-1390  
(REV. 9-2001)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

Az. 2964

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

Unknown 99/980754

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP00/03664

22 April 2000

3 May 1999

TITLE OF INVENTION

METHOD OF GENERATING DEFECTS IN A LATTICE STRUCTURE OF A SEMICONDUCTOR

APPLICANT(S) FOR DO/EO/US MATERIAL

Wilfred Lerch, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☐ Other items or information:

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*Evelyn L. Stump*  
Evelyn L. Stump

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|--|--|--|--|---|--|
| U.S. APPLICATION NO. (if known, see 37 CFR 1.5)<br><b>Unkn 09/980754</b> |  | INTERNATIONAL APPLICATION NO.<br><b>PCT/EP00/03664</b> |  | ATTORNEY'S DOCKET NUMBER<br><b>Az. 2964</b> |  |
|--|--|--|--|---|--|

|  |              |              |            |   |  |
|--|--------------|--------------|------------|---|--|
| 21. <input checked="" type="checkbox"/> The following fees are submitted:<br><b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b><br>Neither international preliminary examination fee (37 CFR 1.482)<br>nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO<br>and International Search Report not prepared by the EPO or JPO ..... <b>\$1040.00</b><br><br>International preliminary examination fee (37 CFR 1.482) not paid to<br>USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$890.00</b><br><br>International preliminary examination fee (37 CFR 1.482) not paid to USPTO<br>but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$740.00</b><br><br>International preliminary examination fee (37 CFR 1.482) paid to USPTO<br>but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$710.00</b><br><br>International preliminary examination fee (37 CFR 1.482) paid to USPTO<br>and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b><br><b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b> |              |              |            | <b>CALCULATIONS PTO USE ONLY</b><br><br><br><br><br><br><br><br><br><br><div style="border: 1px solid black; padding: 2px;">\$ 890.00</div> |  |
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| CLAIMS   | NUMBER FILED | NUMBER EXTRA | RATE       |   |  |
| Total claims   | - 20 =       |              | x \$18.00  | <div style="border: 1px solid black; padding: 2px;">\$</div>  |  |
| Independent claims   | - 3 =        |              | x \$84.00  | <div style="border: 1px solid black; padding: 2px;">\$</div>  |  |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable)  |              |              | + \$280.00 | <div style="border: 1px solid black; padding: 2px;">\$</div>  |  |
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| <input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above<br>are reduced by 1/2.  |              |              |            | <div style="border: 1px solid black; padding: 2px;">\$</div>  |  |
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**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

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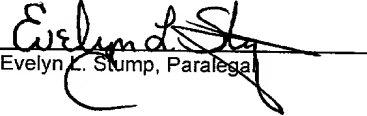
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Evelyn L. Stump, Paralegal

In the Application of Wilfred Lerch, et al.

Ser. No.: Not Yet Known (Based on PCT/EP00/03664 filed April 22, 2000 and German priority documents 199 20 322.9 filed May 3, 1999 and 19927 962.4 filed June 18, 1999)

For: METHOD OF GENERATING DEFECTS IN A GRID STRUCTURE OF A MICONDUCTOR MATERIAL

Filed on: November 3, 2001

Assistant Commissioner for Patents

Washington, DC 20231

**PRELIMINARY AMENDMENT ACCOMPANYING PCT NATIONAL STAGE APPLICATION**

Sir:

Prior to examination, please amend the above-identified application as follows.

**IN THE SPECIFICATION:**

On page 1, immediately after the title, please insert the following heading:

--Background of the Invention--.

On page 3, line 1, please insert the following heading:

--Summary of the Invention--.

On page 8, between lines 10 and 11, please insert the following heading:

--Brief Description of the Drawing--;

On page 9, between lines 17 and 18, please insert the following heading:

--Description of Preferred Embodiments--.

On page 10, line 9, after the word "torr", please insert --"(133 X 10<sup>-6</sup> Pa)"--.

On page 19, at the bottom of the page, please insert the following paragraph:

--The specification incorporates by reference the disclosure of German priority documents 199 20 322.9 filed 03 May 1999, 199 27 962.4 filed 18 June 1999 and International priority document PCT/EP00/03664 filed 22 April 2000.

The present invention is, of course, in no way restricted to the specific disclosure of the specification and drawings, but also encompasses any modifications within the scope of the appended claims.--

**IN THE CLAIMS:**

Please cancel claims 1 - 27, and replace them with the attached claims 28 - 49.


**REMARKS**

Claims 28 - 49 are pending in the application.

Appropriate headings have been added to the specification, and claims from the literal translation have been replaced by claims drafted in conformity with U.S. Patent practice.

The application in its amended state is believed to be in condition for allowance. However, should the Examiner have any comments or suggestions, or wish to discuss the merits of the application, the undersigned would very much welcome a telephone call in order to expedite placement of the application into condition for allowance.

Respectfully submitted,



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WHAT WE CLAIM IS:

28. A method of generating defects in a lattice structure of a semiconductor material during thermal treatment of the material, said method including the steps of:

5                   controlling at least one of a concentration and a distribution of defects or vacancies as a function of a process gas atmosphere; and

                  either producing an  $\text{Si}_x\text{O}_y\text{N}_z$  oxy-nitride layer having a thickness of up to 2nm (20 angstroms) on a surface of a semiconductor, or

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                  prior to a thermal treatment, removing a natural  $\text{SiO}_2$  layer from a surface of a semiconductor and producing an  $\text{Si}_3\text{N}_4$  layer having a thickness of up to 4nm (40 angstroms) on said semiconductor.

15                   29. A method according to claim 28, wherein said defects are vacancies.

30. A method according to claim 28, wherein said defects are semiconductor substrate atoms on interstitial lattice positions.

20                   31. A method according to claim 28, wherein a composition of the process gas is controlled.

32. A method according to claim 28, wherein a concentration of a process gas or of process gas components is controlled.

33. A method according to claim 28, wherein a partial pressure of a process gas is controlled.

34. A method according to claim 28, wherein a process gas includes a nitrogen-containing gas.

5 35. A method according to claim 34, wherein said process gas includes at least one of  $\text{NH}_3$  and  $\text{N}_2$ .

36. A method according to claim 28, wherein a process gas contains no oxygen.

10 37. A method according to claim 28, wherein a process gas includes an oxygen-containing component.

38. A method according to claim 37, wherein said oxygen-containing component includes at least one of  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{H}_2\text{O}$ .

39. A method according to claim 28, wherein a temperature behavior of a thermal treatment is controlled in terms of time.

15 40. A method according to claim 28, wherein said process gas atmosphere contains argon.

41. A method according to claim 35, wherein said process gas includes  $\text{NH}_3$  having a concentration of 0 to 10,000ppm.

20 42. A method according to claim 41, wherein said  $\text{NH}_3$  concentration is 2500 to 5,000ppm.

43. A method according to claim 28, wherein a thermal stressing of a semiconductor wafer is reduced to a minimum.

44. A method according to claim 28, wherein a distribution of foreign atoms within semiconductor material is controlled by means of distribution of said defects.

45. A method according to claim 44, wherein said foreign atoms include at least one of the elements of the group consisting of boron, phosphorus, As, Sb and In.

46. A method according to claim 28, wherein said method is carried out on a semiconductor doped with foreign atoms.

47. A method according to claim 28, wherein said method is carried out on a semiconductor that is to be doped.

48. A method according to claim 47, wherein said semiconductor is doped.

49. A method according to claim 28, wherein doping into said semiconductor is effected by means of at least one of gas phase doping, implantation, and diffusion by out-diffusion from a layer that is in contact with said semiconductor.



5/pst

Method Of Generating Defects in a Lattice Structure  
of a Semiconductor Material

5 The present invention relates to a method of generating defects in a lattice structure of a semiconductor material during thermal treatment of the material.

10 During the treatment of semiconductor materials, it is known to thermally treat the semiconductor materials in order to influence the doping or doping profile of foreign atoms within the semiconductor material.

15 In this connection, it is known, for example, from W. Lerch et al.; Mat. Res. Soc. Symp. Proc. (1998), volume 525, pages 237-255, and D. F. Downey et al.; Mat. Res. Soc. Symp. Proc. (1998), volume 525, pages 263-271, that the doping profile of boron within a semiconductor material can be influenced by means of an oxygen-containing process gas at constant thermal load. The oxygen-containing process gas effects an oxidation of the Si semiconductor material, which leads to a  
20 super saturation of inherent intermediate lattice atoms (Si atoms on intermediate lattice locations), the concentration of which influences the diffusion characteristic of the boron and hence the doping profile.

In general, with the above-described method it is possible to influence essentially only those doping profiles the foreign atoms of which essentially reach a lattice position via the so-called kick-out mechanism. With this mechanism, the foreign atom that was previously located in an interstitial lattice position reaches a lattice position, whereby a silicon (or in general lattice) atom is displaced from its lattice position in the interstitial lattice position.

It is furthermore known that the doping profile of foreign atoms, which form lattice defects within a semiconductor material, can be changed during a thermal treatment by varying the temperature behavior, whereby high thermal stresses are frequently generated within the semiconductor material in order to achieve desired profiles. However, this inherently contains the risk of damage to the semiconductor due to the thermal treatment. Furthermore, the energy consumption for the thermal treatment is very high.

Proceeding from this aforementioned state of the art, it is an object of the present invention to provide a new method which in a simple and economical manner enables a precise control of lattice defects in a semiconductor material.

This object is inventively realized by a method of generating defects in a lattice structure of a semiconductor material during thermal treatment of the material, according to which the defect concentration and/or distribution is controlled as a function of a process gas atmosphere.

5 The above method enables a control of the defect concentration and/or distribution in a lattice structure of a semiconductor material during the thermal treatment thereof at an essentially constant budget (integral of the temperature-time curve). Thus, at a minimal thermal stress, the defect concentration and/or distribution can be controlled as a function  
10 of the process gas atmosphere. The defect concentration and/or distribution in turn influences the concentration as well as the diffusion characteristic of foreign atoms within the semiconductor material.

Pursuant to one preferred specific embodiment of the invention, the defects that are generated are vacancies (empty lattice positions). Due  
15 to the generation of vacancies, foreign atoms can pass to the lattice positions independently of the above mentioned kick-out mechanism. This is particularly advantageous with large foreign atoms such as arsenic or antimony, which essentially pass to lattice positions of the  
20 semiconductor only by filling of vacancies (empty lattice positions).

Pursuant to a further specific embodiment of the invention, the defects are semiconductor atoms on interstitials or intermediate lattice positions that in turn require another mechanism via which the foreign atoms reach lattice positions.

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The defects are advantageously generated in the region of the semiconductor surface with a depth of 0 to approximately 1000 angstroms. The defects are thus also disposed in the region of implanted foreign atoms, as a result of which the distribution and concentration of the foreign atoms are considerably influenced.

10

Pursuant to a particularly preferred embodiment of the present invention, the composition of the process gas is controlled. By means of the composition of the process gas, which can comprise a mixture of several gases, the defect concentration and/or distribution can be controlled in a particularly straightforward, precise and effective manner. The concentration of the process gas or the process gas component is preferably controlled within an inert gas, which functions as a carrier gas.

15

20

The partial pressure of the process gas is preferably controlled.

Pursuant to a particularly preferred embodiment of the invention, the process gas is a nitrogen-containing gas that preferably generates vacancies (empty lattice positions) that considerably influence the doping profile of foreign atoms. In this connection, the process gas is preferably formed of  $\text{NH}_3$  or  $\text{N}_2$ . The nitrogen-containing gas leads to an injection of vacancies via the equilibrium concentration.

The process gas is advantageously provided with no oxygen, especially no free oxygen, which would lead to an oxidation of the semiconductor material and could adversely affect the generation of vacancies (empty lattice positions).  $\text{O}_2$  leads to a self interstitial injection via the equilibrium concentration at the process temperature.

Pursuant to an alternative embodiment, in contrast, the process gas is provided with an oxygen-containing component that can lead to an increase of the defect concentration (self-interstitials). In this connection, the oxygen-containing component preferably comprises  $\text{N}_2\text{O}$ . Pursuant to a further preferred embodiment of the invention, the temperature behavior of the thermal treatment is controlled in terms of time, and the thermal loading of the semiconductor material is preferably reduced to a minimum.

Furthermore, via the control of the temperature behavior of the thermal treatment in terms of time, the diffusion characteristic of the defects as well as of implanted foreign atoms can be controlled. In this regard, in particular the depth of penetration of the lattice defects, vacancies and/or self-interstitials, as well as of the foreign atoms, and thus the spatial distribution thereof within the semiconductor material, can be influenced.

The process gas atmosphere preferably contains argon, which functions as an inert carrier gas.

Pursuant to a preferred embodiment of the invention, an  $\text{Si}_x\text{O}_y\text{N}_z$  layer is generated upon the surface of the semiconductor. The thickness of the layer is preferably between 0 and 20 angstroms.

Pursuant to an alternative specific embodiment of the invention, a natural  $\text{Si}_2\text{O}$  layer is preferably removed from the semiconductor surface prior to the thermal treatment in order to be able to generate an oxide-free surface layer. During the thermal treatment an  $\text{Si}_3\text{N}_4$  layer having a thickness between 0 and approximately 40 angstroms is then preferably generated upon the semiconductor wafer.

Pursuant to a particularly preferred embodiment of the invention, the  $\text{NH}_3$  concentration is between approximately 500 to 10,000ppm. The  $\text{NH}_3$  concentration is preferably between 2500 to 5,000ppm.

5 To avoid damage to the wafer, the thermal stress of the semiconductor wafer during the thermal treatment is preferably reduced to a minimum. At this low thermal stress the defects can advantageously be controlled via the process gas atmosphere.

10 Pursuant to a particularly preferred embodiment of the invention, a concentration and/or distribution of foreign atoms within the semiconductor material is controlled via the concentration and/or distribution of the defects.

15 The foreign atoms are preferably selected from the following group: boron, phosphorus, As, Sb and In, whereby combinations are also possible.

20 Pursuant to one embodiment of the invention, the above method is preferably carried out on an doped semiconductor, as a result of which during the thermal treatment at the same time the concentration and/or

distribution of the foreign atoms is controlled by the defect concentration and/or distribution, i.e. vacancies and/or self-interstitials.

Pursuant to an alternative embodiment of the present invention, the method is carried out on a non-doped semiconductor. In this way, the semiconductor material can be prepared for a subsequent, selected or targeted doping of the semiconductor material, which has a direct influence upon the following treatment processes of the semiconductor.

The invention will be subsequently explained in greater detail with the aid of preferred specific embodiments of the invention in conjunction with the drawings; the drawings show:

Figure 1 the thickness of an oxy-nitride layer as a function of the  $\text{NH}_3$  concentration in an argon atmosphere for an Si wafer that is coated with natural oxide;

Figure 2 schematically the percent of retained dose of foreign atoms in an implanted silicon semiconductor as a function of the  $\text{NH}_3$  concentration for a prescribed temperature-time process control in an RTP system, as well as the correlation of the sheet resistance of the semiconductor as a function of the  $\text{NH}_3$  concentration;



Figure 3 the arsenic distribution in a silicon semiconductor material implanted with arsenic for various  $\text{NH}_3$  concentrations in an inert gas, as a function of the depth of penetration thereof from the wafer surface, for a prescribed course of the temperature-time control of the thermal treatment;

Figure 4 the sheet resistance of a semiconductor after a thermal treatment with prescribed temperature-time controls, as a function of a  $\text{NH}_3$  concentration in argon;

Figure 5 the concentration of arsenic atoms in a silicon semiconductor wafer as a function of the depth of penetration from the substrate surface for various process gas compositions, at the same temperature-time control.

Figure 1 shows the thickness of an oxy-nitride layer as a function of the  $\text{NH}_3$  concentration in an argon atmosphere for a silicon semiconductor wafer that is coated with a natural oxide and that is subjected to a thermal treatment of, for example,  $1000^\circ \text{C}$  for 10 seconds. With the thermal treatment that is the basis of Figure 1, argon was used as the inert carrier gas for the  $\text{NH}_3$  component. The thermal treatment includes heating the semiconductor wafer to, for example,  $1100^\circ \text{C}$  for 10 seconds. In so doing, the oxy-nitride layer is built up during the

thermal treatment. A nitride layer is formed at lesser or also greater temperatures, and the process time is also not fixed.

As can be seen from Figure 1, after the thermal treatment and at very low  $\text{NH}_3$  concentrations (in the range of 0 to 1ppm) or under vacuum conditions (e.g.  $10^{-6}$  torr), the  $\text{Si}_x\text{O}_y\text{N}_z$  layer is less than the original, natural oxide layer thickness which, as can be seen from Figure 1, is approximately 13 angstroms. This is attributable to the fact that at these  $\text{NH}_3$  concentrations, and as a function of the temperature and possible gas impurities (e.g.  $\text{O}_2$ ), an "etching" of the Si wafer takes place. This need, however, not necessarily occur.

As the  $\text{NH}_3$  concentration increases (with the thermal treatment, however, remaining the same), the  $\text{Si}_x\text{O}_y\text{N}_z$  layer increases and reaches a maximum of approximately 20 angstroms in pure  $\text{NH}_3$ . In this connection, it should be noted that the maximum layer thickness is essentially a function of the process control, i.e. of the temperature-time behavior of the process.

For thermal treatments with temperatures below approximately  $1000^\circ\text{C}$ , instead of argon,  $\text{N}_2$  can be used as the inert gas since due to the high bonding energy of  $\text{N}_2$  below  $1000^\circ\text{C}$ , no or only very little nitriding

occurs. At temperatures above 1000° C, N<sub>2</sub> can also be used as a nitriding component in a process gas, for example together with argon or also NH<sub>3</sub>.

5 With the method that forms the basis of Figure 1, a semiconductor wafer having a natural silicon oxide layer was treated. Alternatively, prior to the treatment, however, the natural silicon oxide can also be removed from the wafer, for example by wet etching, VPC (Vapor Phase Cleaning) or some other known method, so that during the  
10 subsequent thermal treatment essentially an Si<sub>3</sub>N<sub>4</sub> layer is formed. The Si<sub>3</sub>N<sub>4</sub> layer thicknesses that can hereby be achieved are in a range of approximately 0 to 40 angstroms, whereby the layer thickness is a function not only of the concentration and the composition of the nitrogen-containing process gas but also of the temperature-time  
15 control of the thermal treatment.

Figure 2 schematically shows the retained dose R<sub>D</sub> of foreign atoms in a doped or implanted silicon semiconductor, as well as the sheet resistance R<sub>S</sub> as a function of the NH<sub>3</sub> concentration after a thermal  
20 treatment having a prescribed temperature-time process control.

Figure 2 schematically shows the retained dose of foreign atoms  $R_D$  (Retained Dose) in the semiconductor (silicon) as a function of the  $NH_3$  concentration (or in general the concentration of a nitrogen-containing process gas component) for a specific temperature-time process control in an RTP system. It is clearly shown that in pure inert gas, a large proportion of the foreign atoms leave the semiconductor by diffusion. This results in a reduction of foreign atoms in the semiconductor. A drawback of this reduction is an increase of the sheet resistance  $R_S$  and under certain circumstances to an unuseability of the overall semiconductor (wafer). By adding one or more nitrogen-containing process gas components, a nitriding occurs on the semiconductor surface that acts as a diffusion barrier for the foreign atoms. As the nitrogen-containing process gas component (or components) increases, the "out diffusion" of the foreign atoms is suppressed.

At higher  $NH_3$  concentrations, the retained dose of foreign atoms increases within the semiconductor wafer and at a concentration of approximately 2500ppm nearly achieves a maximum. This is attributable to the fact that the nitrogen-containing process gas component effects a nitriding on the semiconductor surface that acts as a diffusion barrier for the foreign atoms.

For example, at a concentration of approximately 2500 to 10,000ppm  $\text{NH}_3$  in an inert gas, such as argon, at a temperature-time process of 900° C to 1150° C at a duration of, for example, 10 seconds, the “out diffusion” of foreign atoms in an implanted semiconductor wafer (such as with arsenic or antimony) in silicon is nearly entirely suppressed. This is achieved by an  $\text{Si}_x\text{O}_y\text{N}_z$  or  $\text{Si}_3\text{N}_4$  layer having a thickness of 10 to 16 angstroms (see Figure 1). This is a great advantage, especially with very thin pn junctions, since here a “out diffusion” of foreign atoms would lead to undefined pn junctions having undefined high sheet resistances.

Figure 3 shows by way of example the arsenic distribution of silicon semiconductors implanted with arsenic after a prescribed thermal treatment with a constant thermal budget for different  $\text{NH}_3$  concentrations in argon, as a function of the depth of penetration from the wafer surface. In this connection, the same starting conditions were present.

The distribution for 0ppm  $\text{NH}_3$ , i.e. in the case of conducting the process in pure argon or inert gas, exhibits a considerable reduction of foreign atoms in comparison to the other distributions. This is due to

the "out diffusion" of the arsenic (foreign) atoms described above in conjunction with Figure 2. Such a reduction of foreign atoms leads to a considerable increase of the sheet resistance, as illustrated in Figure 4, which shows the sheet resistance of the semiconductor as a function of the  $\text{NH}_3$  concentration for various temperatures at a process time of 10 seconds. As can be seen from this diagram, the sheet resistance demonstrates a tendency toward small resistances at approximately 10,000ppm  $\text{NH}_3$ , whereby its absolute value is essentially codetermined from the temperature-time process control. The higher the selected temperature, the smaller the sheet resistance. In this connection, the thermal budget is advantageously minimized, i.e. the wafers are preferably processed at a high temperature in order to keep the process duration as short as possible. Typical process temperatures are between 800° C and 1200° C, and typical times are between approximately 0.5s and 360s.

Figure 3 shows that during a treatment of the doped silicon semiconductor in pure argon, the concentration, as well as the depth of penetration of the arsenic, are at their lowest, resulting in a higher  $R_s$  value. As the  $\text{NH}_3$  concentration increases, not only does the arsenic concentration increase but the depth of penetration of the arsenic atoms in the semiconductor wafer also increases.

Figure 3 shows that merely by the selection of the concentration of at least one nitrogen-containing process gas component, at a prescribed temperature-time process, the distribution of the foreign atoms and the depth of penetration of the foreign atoms can be adjusted or established. This provides the possibility, at a minimum still tolerable thermal stress of the semiconductor, to set the foreign atom distribution in wide ranges merely via the process gas composition. In this way, the sheet resistance can be varied up to a factor of approximately 10, and in the same way the depth of penetration of the foreign atoms can be varied approximately by a factor of 2.

Figure 4 shows the sheet resistance of a silicon semiconductor wafer implanted with arsenic as a function of the  $\text{NH}_3$  in an argon carrier gas for various temperatures of the thermal treatment at a respective process time of 10 seconds. It can be recognized that at higher  $\text{NH}_3$  concentrations the sheet resistance is reduced. In this connection, at a concentration greater than approximately 2500 – 5000ppm  $\text{NH}_3$  a saturation or lower threshold value of the sheet resistance to small sheet resistances occurs that cannot be further reduced even if the  $\text{NH}_3$  concentrations rise further. The value of the sheet resistance is similarly essentially codetermined from the temperature-time process

control. In this connection, one can recognize that at higher temperatures the sheet resistance becomes less. Typical process temperatures are between 800° C and 1200° C, and typical steady state times are between 0.5s to 360s. However, to prevent damage to the semiconductor material, the thermal budget should be minimized, in which connection the process times should preferably be under 60 seconds and the temperatures should be between 950° C and 1150° C. With very thin pn junctions, so-called flash processes are utilized that are defined by very high temperature increase rates, between 100° C per second and 500° C per second, as well as a rapid cooling, between approximately 25° C per second to 150° C per second. With these processes, the maximum temperature is frequently maintained for less than five seconds. Often there is even a direct transition from the heating phase into the cooling phase, as a result of which very small thermal budgets can be achieved. However, very high temperatures must be achieved in a very short period of time. At the moment, this can be achieved only with the most modern units, such as the AST 3000 from RTP Systems GmbH, since only with such equipment the power for such high ramp rates is available in a controlled manner, so that a homogeneous heating of the semiconductor substrate is still possible.



Figure 5 again shows the concentration of arsenic atoms in an doped Si semiconductor wafer as a function of the depth of penetration from the substrate surface for various process gas compositions, with the temperature-time processes remaining constant. With the method that forms the basis of Figure 5, in addition to  $\text{NH}_3$  in an argon atmosphere an oxygen-containing component, namely  $\text{N}_2\text{O}$ , was also used.

Figure 5 shows that the addition of  $\text{N}_2\text{O}$  increases the arsenic concentration. This also allows the sheet resistance to be further reduced. Furthermore, Figure 5 shows that the addition of an adequate quantity of  $\text{N}_2\text{O}$  reduces the depth of penetration of the arsenic atoms, which is particularly expedient for thin pn junctions. By adding oxygen-containing gas, the arsenic concentration can be increased by up to approximately twenty times as a function of the concentration of the nitrogen containing gas, whereby the depth of penetration of the foreign atoms is increased only insignificantly, and can if necessary be reduced. In this way, the arsenic distribution can approximate a desired box profile having steeply dropping sides. By the generation of self-defects (vacancies, self-interstitials) on the surface, prescribed dopant profiles (electrically inactive) can be converted into electrically active dopant profiles accompanied by a

minimalization of the depth of penetration and a maximum concentration (so-called box profile).

5 In general one can say that by means of oxygen and/or nitrogen containing gases, independently of whether the wafer is extrinsically doped (implantation, GPD, diffusion by out diffusion of a layer disposed on a semiconductor into the semiconductor) or is not doped, the defect concentration (self-interstitials/vacancies) can be set as desired, also under the influence of the thermal treatment.

10 The present invention has been described with the aid of specific exemplary embodiments, without thereby being limited to these special examples. In particular, for carrying out the method it is not necessary that the process gas atmosphere contain an inert carrier gas. Rather, 15 the method could be carried out under low pressure or partial vacuum conditions, whereby the process gas concentration can be regulated via the pressure. Furthermore, the present invention is not limited to the use of  $\text{NH}_3$  or  $\text{N}_2\text{O}$  as process gas components. Further examples for process gas combinations are, for example,  $\text{NO}$ ,  $\text{H}_2\text{O}$  (water vapor). 20 If  $\text{H}_2\text{O}$  is used, the thermal budget can be reduced still further, and there occurs a lower OED (Oxygen Enhanced Diffusion). The method can also be used for non-doped semiconductors in order to prepare

them for a subsequent treatment, such as an implantation or a doping step.

5

A further exemplary application for the inventive method is also the use upon boron and/or phosphorus and/or antimony and/or indium (or universal acceptors/donators) in order to influence the diffusion characteristic (profile) with oxygen-containing and/or nitrogen-containing gases, and to establish, for example, box profiles.

Patent Claims

1. Method of generating defects in a lattice structure of a semiconductor material during thermal treatment of the material, in which the concentration and/or distribution of defects or vacancies are controlled as a function of a process gas atmosphere.
2. Method according to claim 1, characterized in that the defects are vacancies (empty lattice positions).
3. Method according to claim 1 or 2, characterized in that the defects are semiconductor- substrate atoms on interstitial lattice positions (self-interstitials).
4. Method according to one of the preceding claims, characterized in that the composition of the process gas is controlled.
5. Method according to one of the preceding claims, characterized in that the concentration of the process gas or of the process gas components is controlled.
6. Method according to one of the preceding claims, characterized in that the partial pressure of the process gas is controlled.
7. Method according to one of the preceding claims,

characterized in that the process gas includes a nitrogen-containing gas.

8. Method according to claim 7, characterized in that the process gas includes  $\text{NH}_3$ .

9. Method according to claim 7 or 8, characterized in that the process gas includes  $\text{N}_2$ .

10. Method according one of the preceding claims, characterized in that the process gas contains no oxygen.

11. Method according to one of the claims 1 to 9, characterized in that the process gas includes an oxygen-containing component.

12. Method according to claim 11, characterized in that the oxygen-containing component includes  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and/or  $\text{H}_2\text{O}$ .

13. Method according to one of the preceding claims, characterized in that the temperature behavior of the thermal treatment is controlled in terms of time.

14. Method according to one of the preceding claims, characterized in that the process gas atmosphere contains argon.

15. Method according to one of the preceding claims, characterized in that an  $\text{Si}_x\text{O}_y\text{N}_z$  layer is produced upon the surface of the semiconductor.

16. Method according to claim 15, characterized in that the thickness of the layer is 0 to 20 angstroms.
17. Method according to one of the preceding claims, characterized in that prior to the thermal treatment a natural SiO<sub>2</sub> layer is removed from the semiconductor surface.
18. Method according to claim 17, characterized in that a Si<sub>3</sub>N<sub>4</sub> layer having a thickness of between 0 and 40 angstroms is produced upon the semiconductor.
19. Method according to claim 7, characterized in that the NH<sub>3</sub> concentration is 0 to 10,000ppm.
20. Method according to claim 19, characterized in that the NH<sub>3</sub> concentration is 2500 to 5,000ppm.
21. Method according to one of the preceding claims, characterized in that the thermal stress of the semiconductor wafer is reduced to a minimum.
22. Method according to one of the preceding claims, characterized in that a distribution of foreign atoms within the semiconductor material is controlled via the distribution of the defects.
23. Method according to claim 22, characterized in that the foreign atoms have at least one element of the following group of boron, phosphorus, As, Sb and In.

- 5
24. Method according to one of the preceding claims, that the method is carried out on a semiconductor doped with foreign atoms.
25. Method according to one of the claims 1 to 23, characterized in that the method is carried out on a semiconductor that is to be doped.
26. Method according to claim 25, characterized in that the semiconductor is doped.
- 10
27. Method according to one of the preceding claims, characterized in that the semiconductor is doped by means of gas phase doping, implantation, and/or diffusion by out-diffusion into the semiconductor from a layer that contacts the semiconductor.

Fig. 1

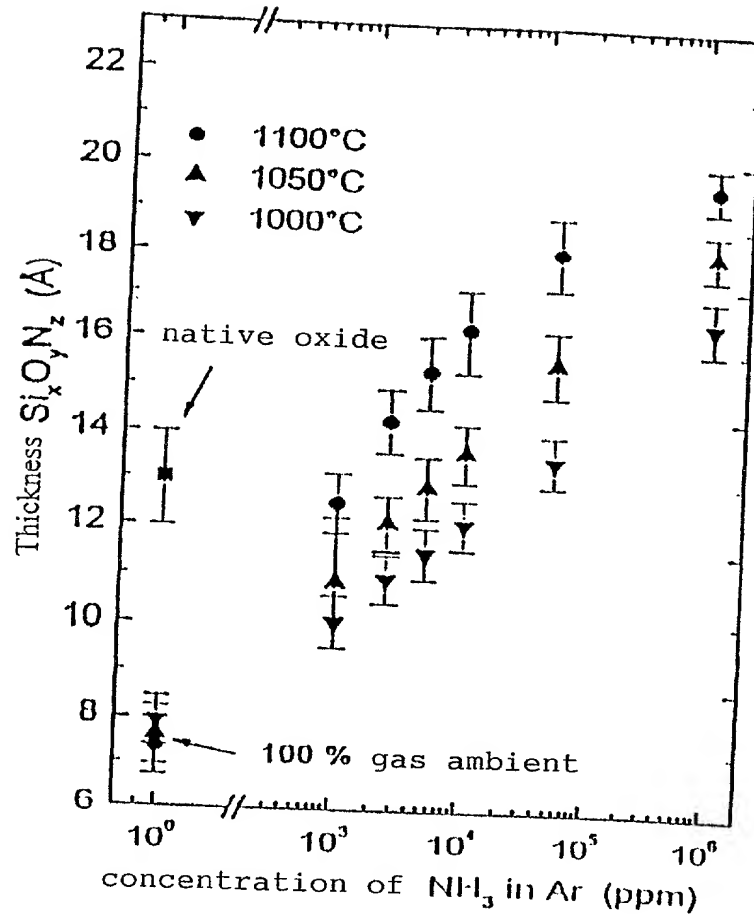




Fig. 2

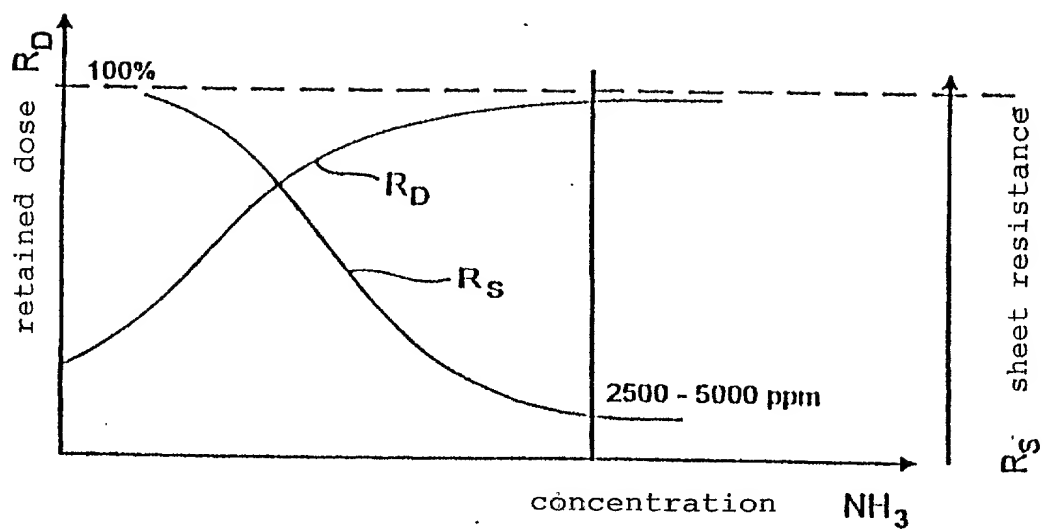


Fig. 3

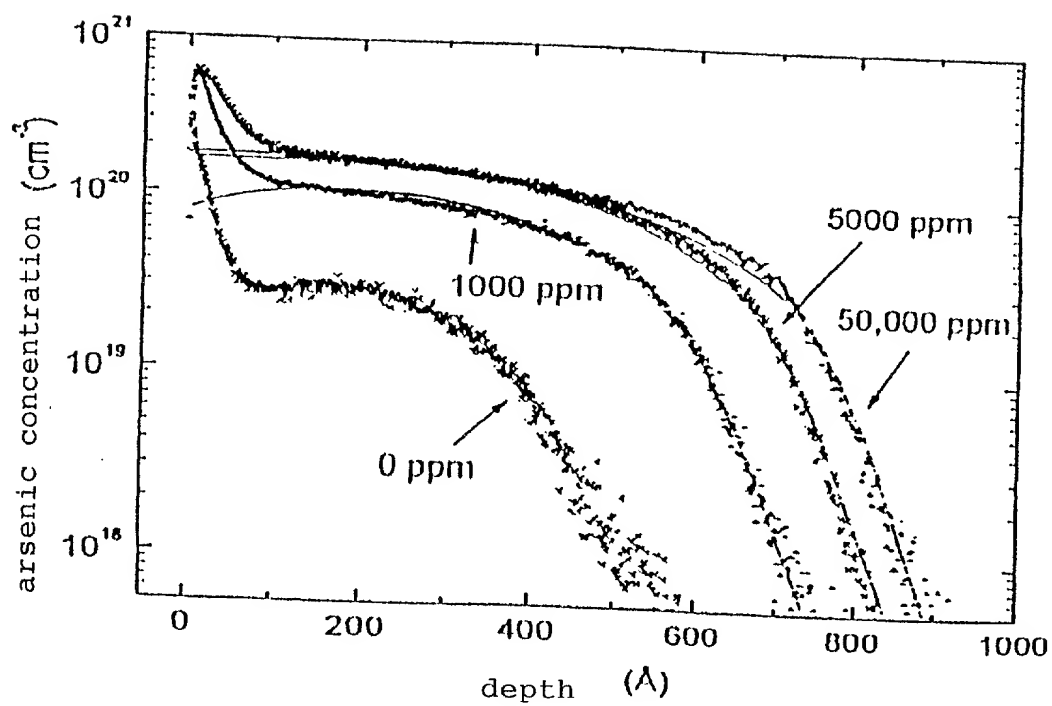


Fig. 4

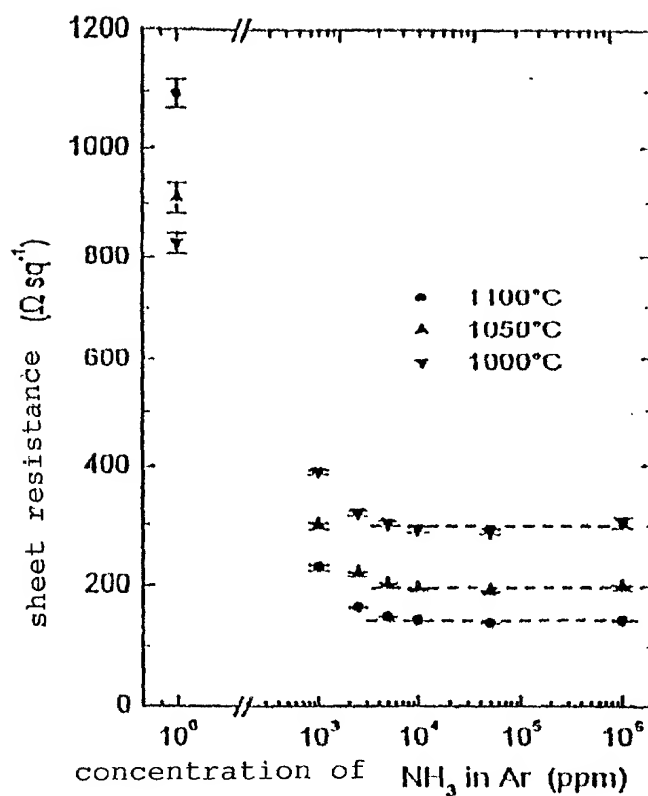
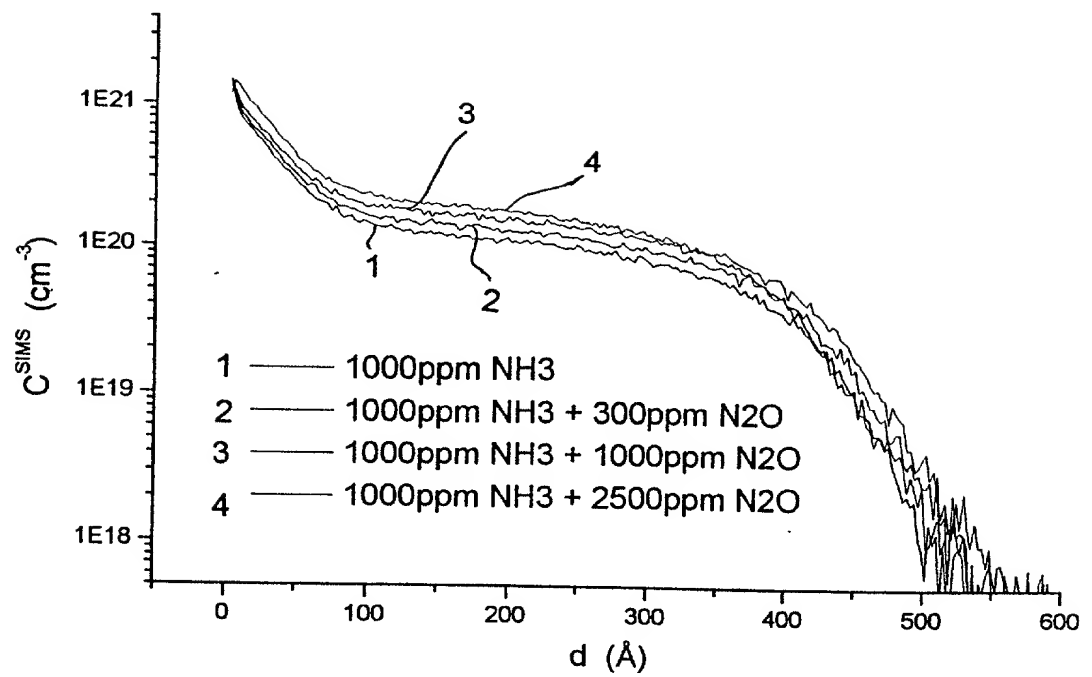


Fig. 5



COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

As below named inventors, we hereby declare that:

Our residences, post office addresses and citizenships are as stated below next to our names; we believe are the original, first and joint inventors of the subject matter which is claimed and for which a patent is sought of the invention entitled:

METHOD OF GENERATING DEFECTS IN A LATTICE STRUCTURE OF A SEMI-CONDUCTOR MATERIAL

the specification of which

\_\_\_\_\_ is attached hereto;  
xx was filed on 22 April 2000 as International Application Ser. No. PCT/EP00/03664 and is amended as Serial No. 09/980,754 filed on November 2, 2001.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information known by me to be material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

| Prior Foreign Applications: |           |                        | Priority Claimed: |    |
|-----------------------------|-----------|------------------------|-------------------|----|
| (Number)                    | (Country) | (Day/Month/Year Filed) | Yes               | No |
| 199 20 322.9                | Germany   | 03 May 1999            | X                 |    |
| 199 27 962.4                | Germany   | 18 June 1999           | X                 |    |

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below:

| (Application Number) | (Filing Date) |
|----------------------|---------------|
|----------------------|---------------|

I hereby appoint attorney, Robert W. Becker, Reg. No. 26,255, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith. Address all telephone calls to (505) 286-3511. Address all correspondence to ROBERT W. BECKER & ASSOCIATES, 707 Highway 66 East, Suite B, Tijeras, New Mexico 87059.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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